O.Z. 6154

Preparation of butene oligomers and tert-butyl ethers from isobutenic C_4 streams

The invention relates to a process for preparing butene
5   oligomers and tert-butyl ethers from C_4 hydrocarbon
streams, by converting the isobutene to butene
oligomers, in particular to isobutene oligomers, and
tert-butyl ethers and removing them from the C_4
streams.

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Isobutene, linear butenes and their subsequent products
are obtained in large amounts from technical C_4 cuts,
for example the C_4 cut from steam crackers or FCC
units. These mixtures consist substantially of
15   butadiene, the monoolefins isobutene, 1-butene and the
two 2-butenes and also the saturated hydrocarbons
isobutane and n-butane. Owing to the small boiling
point differences of the ingredients and their low
separating factors, distillative workup is difficult
20   and uneconomic. Linear butenes and other products are
therefore usually obtained by a combination of chemical
conversions and physical separating operations.

Depending on whether the butenes have a high or low 1-
25   butene content, the C_4 cuts are worked up in different
ways. The first step which is common to all workup
variants is the removal of the majority of the
butadiene. If butadiene can be profitably marketed or
there is an internal demand, it is removed by
30   extraction or extractive distillation. Otherwise, it is
selectively hydrogenated to linear butenes down to a
residual concentration of approx. 2000 ppm by mass. In
both cases, a hydrocarbon mixture (known as raffinate I
or hydrogenated crack-C_4) remains which, in addition to
35   the saturated hydrocarbons n-butane and isobutane,
comprises the olefins isobutene, 1-butene and 2-butenes
(cis and trans).

When the aim is to prepare isobutene and 2-butene or a mixture of linear butenes having a high 2-butene content, preference is given to the following workup sequence: C_4 streams which typically contain not more

5   than 1% of butadiene (C_4 stream from FCC (fluid catalytic cracker), raffinate I or hydrogenated crack-C_4) are hydrogenated and hydroisomerized, i.e. butadiene present is selectively hydrogenated down to a residual content of less than 5 ppm, and 1-butene is at

10   the same time isomerized to 2-butenes. The equilibrium position between 1-butene and the two 2-butenes at 80°C is approx. 1 : 17, i.e. far over to the side of the 2-butenes. Owing to the small boiling point differences, it is possible to obtain only a mixture of isobutene,

15   1-butene and isobutane as the top product, which is worked up in the customary manner, from the hydroisomerization mixture. The bottom product obtained is an isobutene-free mixture which consists of 2-butenes and n-butane. When the hydroisomerization is

20   carried out in a reactive distillation column, virtually 1-butene-free isobutene can be obtained.

When 1-butene is one of the target products, the further procedure may be as follows: isobutene is

25   removed from raffinate I or hydrogenated crack-C_4 by chemical conversion. After the removal of the isobutene, a hydrocarbon mixture (raffinate II) remains which comprises the linear butenes and the saturated hydrocarbons isobutane and n-butane. This mixture can

30   be further separated distillatively, for example into isobutane and 1-butene and a mixture of the two 2-butenes and n-butane. 1-Butene can be obtained in high purity from the 1-butenic fraction in further distillation steps and contains only small amounts of

35   isobutane. This is necessary, since 1-butene is used to a large extent as a comonomer in ethylene polymerization, where isobutene impurities are undesired. Typical specifications of 1-butene therefore

limit the content of isobutene in the 1-butene to less than 1000 ppm.

The chemical conversion of the isobutene can be carried out in water to give the tert-butyl alcohol (TBA). Owing to the low solubility of water in C_4 hydrocarbons, this route is costly and inconvenient and therefore expensive. In addition, it is barely possible to realize complete isobutene removal.

Another possibility is to oligomerize the isobutene and remove the oligomer. A disadvantage is that the complete isobutene removal by oligomerization also converts a large portion of the linear butenes present to co- or homooligomers. A further disadvantage is the partial isomerization of 1-butene to the 2-butenes.

A further possibility for removing isobutene is its reaction with alcohols, for example methanol or ethanol, to give the corresponding tertiary butyl ethers.

The industrially most important process is the reaction of isobutene with methanol to give methyl tert-butyl ether (MTBE) which finds extensive use mainly as a fuel additive.

Owing to the groundwater contamination which has occurred in the USA, an increasingly critical view is taken of the use of tertiary butyl ethers, in particular MTBE, as an octane number improver in gasoline fuels. It cannot be ruled out that the current and future discussions will lead to restriction of the use of tertiary butyl ethers in fuels.

Since the use of butyl ethers as fuel additives will not take up the entire amount of isobutene in the future, there is interest in other methods of removing

isobutene from C_4 mixtures with chemical conversion. The preparation of oligomers of isobutene and their removal from the remaining C_4 mixture is a promising possibility.

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EP 0 048 893 describes a process for coproducing isobutene oligomers and alkyl tert-butyl ethers from C_4 cuts in a reactor. The catalyst used is an acidic ion exchange resin whose exchange sites are partly occupied
10 by metals of the seventh and eighth transition groups of the Periodic Table of the Elements in elemental form (oxidation state 0). The products and the unconverted C_4 hydrocarbons are separated distillatively. In this process, approximately 8% of the linear butenes are
15 lost by oligomerization. The loss of 1-butene is 7%. However, the main disadvantage of this process is that complete isobutene conversion is not achieved, so that the isobutene content in the C_4 hydrocarbon fraction removed is too high to obtain on-spec 1-butene
20 therefrom.

US 5 723 687 likewise describes a process for coproduction of isobutene oligomers and MTBE or ETBE by reaction of a C_4 cut, for example raffinate I, in the
25 presence of methanol or ethanol over an acidic ion exchange resin in a reactor. The losses of 1-butene are not disclosed. A disadvantage of this process is the low isobutene conversion which, according to the examples, is only between 78 and 94%.
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The use of modified ion exchangers for oligomerizing isobutene is disclosed in DE 101 13 381. However, the isobutenic streams used here contain virtually no further unsaturated compounds such as n-butenes.
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DE 29 44 457 describes a process for coproducing isobutene oligomers and MTBE from C_4 hydrocarbon cuts, for example raffinate I. In a first reaction step, from

50 to 90% of the isobutene is oligomerized over a strongly acidic catalyst. The remaining isobutene is reacted with methanol in a second reaction step to give MTBE. The reaction products and the unconverted C_4

5 hydrocarbons are removed distillatively. This process has the following disadvantages:

a) Over 30% of the linear butenes are lost by oligomerization.

b) The losses of 1-butene by oligomerization and

10   isomerization are more than 33%.

c) The isobutene content in the remaining C_4 hydrocarbon mixture is over 0.7%, i.e. highly pure 1-butene having an isobutene content of less than 1000 ppm cannot be prepared from this mixture.

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Since the abovementioned processes are unsatisfactory with regard to the 1-butene yield and/or the isobutene content in the C_4 hydrocarbon mixture (raffinate II) removed, it is an object of the present invention to

20 develop an improved process.

It has now been found that isobutene can be fully removed from a substantially butadiene-free C_4 hydrocarbon stream with only small losses of linear

25 butenes, by oligomerizing a portion of the isobutene in a first reaction step over acidic catalysts whose activity has been modified by the addition of moderators or ion exchange, and removing the remaining isobutene in a second reaction step by reacting with

30 alcohol to give a tert-butyl ether in a reactive distillation column.

In contrast to the existing processes, only a small portion of the 1-butene present in the mixture is lost

35 by isomerization to the 2-butenes.

The present invention therefore provides a process for coproducing butene oligomers and tert-butyl ethers from isobutenic C_4 streams by

a) partly oligomerizing the isobutenic C_4 streams over an acidic catalyst to give butene oligomers and subsequently

b) etherifying the remaining isobutene with an alcohol under acidic catalysis to give tert-butyl ethers,

which comprises
carrying out the etherification under acid catalysis in stage b) in at least two reaction stages, of which at least the last reaction stage is carried out as a reactive distillation.

For the purposes of the present invention, butene oligomers are in particular isobutene oligomers such as di-, tri- or tetramers of isobutene. To a slight extent, these may also comprise cooligomers with or of 1- or 2-butenes.

The butene oligomers prepared according to the invention preferably comprise more than 90% of isobutene oligomers, and the oligomer mixture more preferably has

90 — 97% of isobutene oligomers

1 — 8% of iso- and n-butene cooligomers and

0.1 — 2% of n-butene oligomers.

With the aid of the process according to the invention, it is possible from C_4 streams to produce not only the products of value tert-butyl ether and isobutene oligomers, but also isobutene-free residual streams which are suitable for preparing 1-butene. In addition to the unconverted constituents of the C_4 feed (in general C_4 aliphatics), the isobutene-free residual streams only contain n-butenes, i.e. 1-butene, cis-2-butene and trans-2-butene. It is possible to remove 1-

butene from this mixture distillatively (any i-butane removed together with the 1-butene can be removed from 1-butene in a second distillation step). The remaining 2-butenes which may in some cases still contain 1-
5   butene are in turn valuable feedstocks for preparing linear butene oligomers where the presence of isobutene would lead to undesirably high degrees of branching.

Suitable isobutenic C_4 streams are, for example, light
10   petroleum fractions from refineries, C_4 fractions from crackers (for example steam crackers, hydrocrackers, catalytic crackers), mixtures from Fischer-Tropsch syntheses, mixtures from the dehydrogenation of butanes, mixtures of skeletal isomerization of linear
15   butenes and mixtures resulting from metathesis of olefins. These techniques are described in the literature, cf. K. Weissermel, H.J. Arpe, Industrielle Organische Chemie, Wiley-VCH, 5th edition, 1998, page 23-24; 65-99; 122-124.
20
Preference is given to using C_4 fractions from steam crackers which are primarily operated to produce ethene and propene and in which the raw materials used are, for example, refinery gases, naphtha, gas oil, LPG
25   (liquefied petroleum gas) and NGL (natural gas liquid), or catalytic crackers. Depending on the cracking process, the by-produced C_4 cuts contain different amounts of isobutene. Further main constituents are 1,3-butadiene, 1-butene, c-2-butene, t-2-butene, n-
30   butane and i-butane. In the case of C_4 fractions from steam crackers, typical isobutene contents in the C_4 fraction are from 18 to 35%, and in the case of FCC catalytic crackers are from 10 to 20%.

35   For the process according to the invention, it is advantageous to remove polyunsaturated hydrocarbons such as 1,3-butadiene from the starting mixture. This can be effected by known processes, for example by

extraction, extractive distillation or complex formation (cf. K. Weissermel, H.J. Arpe, Industrielle Organische Chemie, Wiley-VCH, 5th edition, 1998, page 119-121).

An alternative to the removal of the polyunsaturated hydrocarbons is a selective chemical conversion. For example, 1,3-butadiene can be selectively hydrogenated to linear butenes, as described, for example, in EP 0 523 482. The 1,3-butadiene can also be at least partly removed by selective conversions of the 1,3-butadiene, for example dimerization to cyclooctadiene, trimerization to cyclododecadiene, polymerization or telomerization reactions. In all cases in which a crack-C_4 cut has been used as the raw material, a hydrocarbon mixture (raffinate I or hydrogenated crack-C_4 (HCC$_4$)) remains which comprises mainly the saturated hydrocarbons n-butane and isobutane, and the olefins isobutene, 1-butene and 2-butenes.

In the process according to the invention, preference is given to catalytically hydrogenating the polyunsaturated hydrocarbons contained in the isobutenic C_4 streams before the oligomerization in stage a). The polyunsaturated hydrocarbons are mainly 1,3-butadiene; 1,2-butadiene, butenyne and 1-butyne, if at all, are present in a distinctly smaller amount. The hydrogenation can be effected in a one- or multistage hydrogenation process in the liquid phase over a palladium catalyst. To reduce the 1,3-butadiene content to below 1000 ppm, a moderator which increases the selectivity of the palladium catalyst is added in the last stage of the hydrogenation. The moderator used is preferably carbon monoxide which is added in a proportion of from 0.05 to 100 ppm by weight. The content of polyunsaturated hydrocarbons in the feed to this stage should preferably be below 1%, preferably below 0.5%. In the literature, this type of selective

hydrogenation of remaining 1,3-butadiene is known as the SHP (selective hydrogenation process) (cf. EP 0 081 041; Erdöl, Kohle, Erdgas, Petrochem. 1986, 39, 73).

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When amounts greater than 1% of polyunsaturated hydrocarbons such as 1,3-butadiene are present in the isobutenic C_4 streams, they are converted in preceding hydrogenations. These hydrogenations are preferably

10 carried out in the liquid phase over a palladium catalyst. Depending on the content of unsaturated hydrocarbons, the hydrogenation can be carried out in a plurality of stages. For converting crack-C_4 from a steam cracker having a typical 1,3-butadiene content of

15 38 - 45%, a two-stage conversion of the hydrogenation has proven useful. In this case, individual or all stages can be provided with partial product recycling. In this way, 1,3-butadiene concentrations in the effluent of less than 1% are obtainable, so that a

20 further conversion can be effected in an SHP stage.

The hydrocarbon mixtures comprising isobutene and linear butenes used in the process according to the invention preferably have the following compositions:

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Table 1

Typical compositions of hydrocarbon mixtures which are used in the process according to the invention

Component	Steam cracker		Steam cracker		Catalytic cracker	
	HCC_4	HCC_4/SHP	Raff.I	Raff.I/SHP	CC_4	CC_4/SHP
isobutane [% by wt.]	1-4.5	1-4.5	1.5-8	1.5-8	37	37
n-butane [% by wt.]	5-8	5-8	6-15	6-15	13	13
t-butene [% by wt.]	18-21	18-21	7-10	7-10	12	12
1-butene [% by wt.]	35-45	35-45	15-35	15-35	12	12
isobutene [% by wt.]	22-28	22-28	33-50	33-50	15	15
c-butene [% by wt.]	5-9	5-9	4-8	4-8	11	11
1,3-butadiene [ppm]	500-5000	0-50	50-8000	0-50	<10 000	0-50

Explanation:
-     HCC_4: typical of a C_4 mixture which is obtained from the crack-C_4 of a steam cracker (high severity) after the hydrogenation of the 1,3-butadiene without additional moderation of the catalyst.
-     HCC_4/SHP: HCC_4 composition in which 1,3-butadiene residues have been further reduced in an SHP.
-     Raff.I (raffinate I): typical of a C_4 mixture which is obtained from the crack-C_4 of a steam cracker (high severity) after the removal of the 1,3-butadiene, for example by an NMP extractive rectification.
-     Raff.I/SHP: Raff.I composition in which residues of 1,3-butadiene have been further reduced in an SHP.
-     CC_4: typical composition of a crack-C_4 which is obtained from a catalytic cracker.
-     CC_4/SHP: CC_4 composition in which 1,3-butadiene residues have been further reduced in an SHP.

Among others, raffinate I or HCC_4 is an isobutenic hydrocarbon mixture used with preference for the purposes of this invention. However, since plants for

5   working up C_4 hydrocarbons are generally constructed as a chain (combination of a plurality of plants), it is possible that the raffinate I or HCC_4 passes through one or more other process stages before entry into the process according to the invention. In this way, an

10 individually adapted overall plan for workup can be realized in each case with the appropriate product portfolio.

Typical process stages which may precede the process

15 according to the invention are water scrubbing, purification on adsorbers, selective hydrogenation, TBA synthesis, drying and distillation.

Water scrubbing

20 Water scrubbing can be used to fully or partly remove hydrophilic components from the hydrocarbon mixture comprising isobutene and linear butenes, for example nitrogen components. Examples of nitrogen components are acetonitrile or N-methylpyrrolidone (which may

25 result, for example, from a 1,3-butadiene extractive distillation). Oxygen compounds (for example acetone from FCC crackers) can also be partly removed by water scrubbing. The isobutenic hydrocarbon stream is saturated with water after water scrubbing. In order to

avoid biphasicity in the reactor in the subsequent process steps, the reaction temperature there should be approximately 10°C above the temperature of the water scrubbing.

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Adsorbers

Adsorbers are used in order to remove impurities. This may be advantageous, for example, when noble metal catalysts are used in one of the process steps. Often, nitrogen or sulfur compounds are removed by upstream adsorbers. Examples of adsorbers are aluminas, molecular sieves, zeolites, activated carbon, clay earths impregnated with metals. Adsorbers are sold by various firms, for example Alcoa (Selexsorb®).

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Selective hydrogenation (SHP)

Polyunsaturated compounds still present in small amounts, in particular 1,3-butadiene, are further depleted by further selective hydrogenation (cf. EP 0 081 041; Erdöl, Kohle, Erdgas, Petrochem. 1986, 39, 73). The SHP can be operated either as part of a butadiene hydrogenation (see above), or as an independent process step.

25 **TBA synthesis**

Portions of the isobutene can be reacted with water to give tert-butanol (TBA). Processes for preparing TBA from isobutenic hydrocarbon mixtures form part of the prior art (cf., for example, Erdöl, Erdgas, Kohle, 1987, 103, 486). TBA is, for example, used as a solvent, but is also used for preparing highly pure isobutene by dissociation to give isobutene and water.

Drying

35 Any water present in the isobutenic hydrocarbon mixture which may, for example, stem from the water scrubbing or TBA synthesis can be removed by known processes for drying. Suitable processes are, for example, the

distillative removal of water as an azeotrope. Often, an azeotrope with C_4 hydrocarbons present can be utilized or azeotroping agents are added.

The drying of the hydrocarbon mixture may be
5   advantageous for various reasons, for example reduction of the formation of alcohols (mainly tert-butyl alcohol) in the oligomerization/etherification, prevention of (uncontrolled) water moderation in the butene oligomerization, avoidance of technical problems
10 by separation of water or ice at low temperatures (for example intermediate storage).

Distillation

Distillation steps can be used, for example, to remove
15 impurities (for example low boilers such as C_3 hydrocarbons, high boilers such as C_5 hydrocarbons) or to obtain fractions having different isobutene concentrations. This can be effected directly with the raffinate I or the HCC_4, or after passing through one
20 or more other process stages. Direct distillation of the raffinate I or of the HCC_4 makes possible, for example, a separation into a 2-butenes- and n-butane-depleted, isobutene-richer fraction.

25 **Inventive oligomerization of stage a**

The partial oligomerization in stage a) of the isobutene can in principle be carried out homogeneously, i.e. using catalysts soluble in the reaction mixture, or heterogeneously, i.e. using
30 catalysts insoluble in the reaction mixture. The disadvantage of the homogeneous processes is that the catalyst leaves the reactor with the reaction products and unconverted reactants, from which it has to be removed, worked up and disposed of or recycled.

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Owing to the cost and inconvenience of the separation, the partial oligomerization of the isobutene is preferably carried out over solid heterogeneous

catalysts which are additionally often arranged in a
fixed bed, so that a costly and inconvenient catalyst
removal is unnecessary.

5   Useful solid catalysts are acidic materials which are
insoluble in the reactant/product mixture. Most of
these catalysts belong to one of the following groups:
a) mineral acids (e.g. sulfuric acid or phosphoric
   acid) on a support material (e.g. alumina or silica)
10 b) zeolites or other aluminosilicates, undoped or doped
   with other metals, in particular with transition
   metals,
c) acidic ion exchange resins

15 Owing to the high selectivity for the formation of
isobutene oligomers and owing to the minor formation of
by-products, preference is given to using acidic ion
exchange resins as catalysts.

20 Suitable ion exchange resins are, for example, those
which are prepared by sulfonating phenol/aldehyde
condensates or cooligomers of aromatic vinyl compounds.
Examples of aromatic vinyl compounds for preparing the
cooligomers   are   styrene,   vinyltoluene,
25 vinylnaphthalene,   vinylethylbenzene,   methylstyrene,
vinylchlorobenzene,   vinylxylene and divinylbenzene. In
particular, the cooligomers which result from reaction
of styrene with divinylbenzene are used as a precursor
for the preparation of ion exchange resins having sulfo
30 groups. The properties of these resins, in particular
specific surface area, porosity, stability, swelling or
shrinkage and exchange capacity, can be varied via the
preparation process. The resins can be prepared in a
gellike, macroporous or spongelike form. Strongly
35 acidic resins of the styrene-divinylbenzene type are
sold, inter alia, under the following tradenames: CT
151 from Purolite, Amberlyst 15, Amberlyst 35,

Amberlite IR-120, Amberlite 200 from Rohm & Haas, Dowex M-31 from DOW, K 2611, K 2431 from Bayer.

The ion exchange capacity of the resins when entirely in the H$^+$ form is typically between 1 and 2 mol, in particular from 1.5 to 1.9 mol, of H$^+$ per liter of moist resin (as obtained commercially).

In the process of the invention, preference is given to using macroporous resins, for example K 2431 from Bayer, Amberlyst 15 or Amberlyst 35 from Rohm & Haas. The pore volume is preferably from 30 to 60 ml/g, in particular from 40 to 50 ml/g (based on commercial moist resin).

The particle size of the resin is preferably between 500 μm and 1500 μm, in particular between 600 μm and 1000 μm.

The particle size distribution selected may be narrow or wide. For example, ion exchange resins having very uniform particle size (monodisperse resins) can be used.

It may be advantageous to use relatively large particles to reduce the pressure differential in reactors which are flowed through at high linear rates, and to use relatively small particles to achieve the optimum conversion in reactors which are flowed through at a low linear rate.

Optionally, the ion exchange resins can be used in the form of shaped bodies, for example cylinders, rings or spheres.

The acidic ion exchange resin is advantageously adjusted to an activity which does enable the oligomerization of isobutene but barely catalyzes the cooligomerization of isobutene with linear butenes, the

oligomerization of the linear butenes or the isomerization of the linear butenes. Also, the heat evolution in the reactor is adjusted to a value which can be safely controlled from a technical point of

5   view.

The desired catalyst activity can be adjusted with the aid of moderators. These materials are passed over the catalyst together with the reactant. Examples of useful

10   moderators include water, alcohols such as tert-butyl alcohol (TBA), methanol, isononanol or ethanol or ethers such as tert-butyl methyl ether (MTBE), either as a pure substance or mixtures. Preference is therefore given to carrying out the oligomerization in

15   stage a) in the presence of these moderators. In this connection, useful molar ratios have proven to be from 0.01 to 5 mol, preferably from 0.01 to 1 mol, in particular from 0.01 to 0.7 mol, of moderator per mole of isobutene.

20

In the process according to the invention, it is advantageous to use that alcohol which is used for etherifying isobutene in the second reaction step or the ether formed in the second reaction step as the

25   moderator, for example methanol or MTBE.

Also used for oligomerization in the process according to the invention are solid sulfonated ion exchange resins which have the desired activity without the

30   addition of moderators. These are in particular partly neutralized ion exchange resins in which from 1 to 60%, preferably from 1 to 30%, most preferably from 5 to 15%, of the acidic protons of the sulfonic acid groups have been exchanged for metal ions. Metal ions which can

35   replace the protons include alkali metal, alkaline earth metal, transition metal ions (group 1 - 12 metal ions such as chromium, manganese, iron, cobalt, nickel, zinc ions) and aluminum ions, and also ions of the lanthanide

group (rare earths). Preference for this purpose is given to using alkali metal ions, in particular sodium ions. It is also possible that the ion exchange resin is laden with two or more different metal ions.

For the preparation of the partially neutralized ion exchange resins, it is possible to apply different processes which are all described in the technical literature. When the ion exchange resin is in the H^+ form, protons can be exchanged for metal ions. When the resin is in the metal salt form, metal ions can be replaced by protons with the aid of acids. In principle, this ion exchange can be effected either in organic or aqueous suspension.

In a simple process, for example, the ion exchange resin in the H^+ form is slurried with sufficient liquid to result in a readily stirrable suspension. A solution which contains the desired ions is metered in. After completed ion exchange, the ion exchange resin which has been partially exchanged is washed and dried.

The amount of solvent for slurrying the ion exchange resin is typically from one to ten times the intrinsic volume of the ion exchange resin. For the preparation of the solution of the desired type of ion which is metered in, it is advisable to select a solvent which is miscible with the solvent in which the resin is suspended. It is advantageous to use the same solvent.

The ion exchange is preferably effected within the temperature range of from 10 to 100°C, more preferably from 20 to 40°C. The exchange is generally complete after 24 hours at the latest. After the ion exchange, the catalyst is separated from the solution, for example by decanting or filtering, and then optionally washed with a solvent. It is advantageous to use the same solvent in which the catalyst was suspended.

It is advantageous to dry the moist catalyst, firstly to make it easier to handle (more free-flowing) and secondly to keep the contamination of the product by the adhering solvent or its subsequent products low in the first days after the startup of the reactor. The drying can be effected under reduced pressure or in an inert gas stream, for example in a nitrogen stream. The drying temperatures are typically between 10 and 120°C.

A preferred route for preparing the catalysts used in the process according to the invention is the exchange of protons for metal ions in the aqueous phase, washing the partly exchanged ion exchange resin with water and subsequent drying.

The ions with which the resin is to be laden may be solutions of hydroxides, or salts of organic or inorganic acids. In the case of salts of polybasic acids, it is also possible to use acidic salts. It is likewise possible to use compounds with other organic radicals, for example alkoxides or acetylacetonates. Preferred sources of the metal ions are metal hydroxides and salts of inorganic acids. Very particular preference is given to the use of alkali metal hydroxides (e.g. sodium hydroxide), alkali metal halides (e.g. sodium chloride), alkali metal sulfates (e.g. sodium sulfate), alkali metal nitrates (e.g. sodium nitrate), alkaline earth metal hydroxides and alkaline earth metal nitrates.

Depending on the degree of exchange, ion type and resin, the above-described method can be used to prepare catalysts of different activity and selectivity.

A reactor in the process according to the invention may contain a mixture of ion exchange resins of different

reactivity. It is equally possible that a reactor
contains catalysts of different activity arranged in
layers. When more than one reactor is used, the
individual reactors may be charged with catalysts of
5   the same or different activity.

For the industrial performance of the conversion of the
isobutenic hydrocarbon mixtures, various variants are
possible. The conversion may be carried out batchwise
10   or preferably in continuous reactors which are
typically used in solid/liquid contact reactions. When
continuous flow reactors are used, a fixed bed is
usually, but not exclusively, used. An example of a
different concept to fixed bed reactors are reactors in
15   which the ion exchanger is suspended in a liquid phase
(cf. "Bayer process", Erdöl und Kohle, Erdgas,
Petrochemie, 1974, 27, Volume 5, page 240).

When a fixed bed flow reactor is used, the liquid can
20   flow upward or downward. Preference is usually given to
the liquid flowing downward. A cooling liquid flowing
around the reactor may optionally have the same or
opposite flow direction. It is also possible to operate
the reactor with product recycling or in straight pass.
25

When using tubular reactors, the ratio of length to
diameter of the catalyst bed can be varied, either via
the geometric dimensions of the reactor or via its fill
level. At the same amount of catalyst and liquid hourly
30   space velocity (LHSV), different superficial velocities
can therefore be achieved.

The reactors used in the industrial process may be
operated adiabatically, polytropically or virtually
35   isothermally. Virtually isothermally means that the
temperature at an arbitrary point in the reactor is a
maximum of 10°C higher than the temperature at the
reactor entrance. In the case of adiabatic operation of

the reactors, it is generally sensible to arrange a plurality of reactors in series and to cool between the reactors. Reactors which are suitable for polytropic or virtually isothermal operation are, for example, tube
5 bundle reactors, stirred tanks and loop reactors.

It is possible to combine a plurality of reactors, also of different designs. It is additionally possible to operate reactors with recycling of product.
10

The temperatures at which the oligomerization is conducted are between 5 and 160°C, preferably between 40 and 110°C.

15 The conversion can be effected with and without addition of a suitable solvent. Preferred solvents are saturated hydrocarbons, in particular C_4, C_8 or C_{12} hydrocarbons. Very particular preference is given to using isooctane. When solvents are added, their content
20 is from 0 to 60% by weight, preferably from 0 to 30% by weight.

The conversion according to the invention can be carried out at a pressure equal to or greater than the
25 vapor pressure of the starting hydrocarbon mixture at the particular reaction temperature, preferably at a pressure of less than 40 bar, i.e. the isobutenic hydrocarbon mixtures are entirely or partly in the liquid phase during the oligomerization. When the
30 reaction is to be carried out entirely in the liquid phase, the pressure should be from 2 to 4 bar higher than the vapor pressure of the reaction mixture, in order to avoid evaporation problems in the reactors.

35 Even when the reaction is conducted at a pressure at which the reaction mixture is not entirely liquid (for example in a reactive distillation or in process variants similar to US 5 003 124), the oligomerization

in the process according to the invention takes place nonetheless in the liquid phase, i.e. over a "moist", i.e. liquid-wetted, catalyst.

5 The overall conversion of isobutene to oligomers can be adjusted via the amount and type of the catalyst used, the reaction conditions set and number of reactors. In the process according to the invention, from 50 to 95% of the isobutene contained in the reactant, in
10 particular from 60 to 90%, is oligomerized.

The reaction mixture of the partial isobutenic oligomerization can be worked up in different ways. The mixture is either passed directly to the etherification
15 or the butene oligomers are removed before etherification. The oligomers and any hydrocarbons having from 5 to 7 carbon atoms are advantageously removed by distillation.

20 The removed oligomer fraction contains mainly C_8 hydrocarbons. In addition to the diisobutene, this may also contain codimers and higher oligomers (C_{12}, C_{16}). This fraction can be separated in further distillation steps. For example, it is possible to remove a fraction
25 of highly pure diisobutene, in order to use this separately, for example for chemical syntheses. For use as a fuel component for gasoline engines, it may be necessary to remove high-boiling components (boiling point preferably >220°C).
30

It is also possible to fully or partly hydrogenate the butene oligomers, in particular the C_8-olefins. Methods for hydrogenating the products of oligomerization to the corresponding paraffins are sufficiently well known
35 to those skilled in the art. Common methods for hydrogenating olefins are described, for example, in F. Asinger, "Chemie und Technologie der Monoolefine",

Akademie Verlag, Berlin, 1957, page 626 - 628 or DE 197 19 833.

In a preferred embodiment, the hydrogenation is carried out in the liquid phase over a solid catalyst insoluble in the material to be hydrogenated. Preferred hydrogenation catalysts are supported catalysts which consist of an inorganic support and, as the active metal, contain platinum and/or palladium and/or nickel. The temperature at which the hydrogenation is carried out is preferably in the range from 10 to 250°C and the pressure between 1 and 100 bar.

After the hydrogenation, further fractions can be obtained by distillative separation. It is possible to obtain fuel additives having definite properties from these and from the unhydrogenated fractions by blending. Some fractions can also be used as solvents.

The isobutene-depleted C_4 hydrocarbon mixture is converted in a second reaction step (stage b) in the process according to the invention, in which the remaining isobutene is removed by addition of alcohol to give the corresponding tertiary ether. If required, additional low-isobutene C_4 hydrocarbons (for example raffinate II, optionally bought in) may also be added to this C_4 hydrocarbon mixture. These streams may stem from other processes, for example a TBA synthesis or an isobutene removal by hydroisomerization/distillation (cf. EP 1 184 361).

The etherification of the isobutene is carried out as an acid-catalyzed reaction.

The alcohols used therefor are primary, secondary, mono- or polyhydric alcohols having from 1 to 5 carbon atoms, preferably methanol or ethanol.

In order to achieve virtually complete conversion of the remaining isobutene, the addition of the alcohol to

the isobutene is carried out in the presence of an acidic catalyst in at least two reaction stages, of which the last reaction stage is carried out as a reactive distillation. In the prereactor(s), a reaction
5   mixture of the low-isobutene C_4 stream and alcohol is prepared over an acidic catalyst and is in the vicinity of the thermodynamic equilibrium with regard to its isobutene, alcohol and tert-butyl ether concentration. For methanol/MTBE, for example, this is generally
10 between 94 and 96% isobutene conversion. This mixture is fed into the reactive distillation column, where a further portion of the isobutene is converted to the ether.

15 The prereactor or prereactors in which the alcohol is reacted with the isobutene up to close to the thermodynamic equilibrium may be conventional fixed bed reactors (tube bundle reactors, circulation reactors). They may be operated with or without partial recycling,
20 optionally with cooling of the recycle stream.

The reactors are typically operated at from 30 to 110°C and from 5 to 50 bar$_{abs}$. (bara). Since the thermodynamic equilibrium between alcohol/isobutene and ether at low
25 temperature lies substantially to the side of the ether, preference is given when using a plurality of prereactors to operate the first of the reactors at higher temperature (high reaction rate) than the following (utilization of equilibrium point).
30
The catalyst used both in the prereactor and in the reactive distillation column is a solid material which is soluble neither in the feedstock mixture nor in the product mixture and has acidic centers on its surface.
35 The catalyst must not give off any acidic materials to the product mixture under the reaction conditions because this would lead to yield losses.

In the reactive distillation column, the catalyst is either integrated in the packing, for example KataMax® (EP 0 428 265), KataPak® (EP 0 396 650) or MultiPak® (utility model No. 298 07 007.3) or polymerized to shaped bodies (US 5 244 929).

The rule for the activity of the catalysts is that they effect the addition of alcohol to isobutene under the reaction conditions but hardly effect the addition to linear butenes. They must also barely catalyze the oligomerization of linear butenes and dialkyl ether formation from two molecules of the alcohol used. With regard to a high yield of 1-butene, the activity for the attainment of equilibrium between the linear butenes should be low.

Examples of useful solid catalysts include zeolites, acid-activated bentonites and/or clay earths, sulfonated zirconium oxides, montmorillonites or acidic ion exchange resins.

A preferred group of acidic catalysts in the process according to the invention are solid ion exchange resins having sulfonic acid groups. Suitable ion exchange resins are, for example, those which are prepared by sulfonating phenol/aldehyde condensates or cooligomers of aromatic vinyl compounds. Examples of aromatic vinyl compounds for preparing the cooligomers are styrene, vinyltoluene, vinylnaphthalene, vinylethylbenzene, methylstyrene, vinylchlorobenzene, vinylxylene and divinylbenzene. In particular, the cooligomers which result from reaction of styrene with divinylbenzene are used as a precursor for the preparation of ion exchange resins having sulfonic acid groups. The resins can be prepared in a gellike, macroporous or spongelike form. Strongly acidic resins of the styrene-divinylbenzene type are sold, inter alia, under the following tradenames: Duolite C20,

Duolite C26, Amberlyst A15, Amberlyst A35, Amberlite
IR-120, Amberlite 200, Dowex 50, Lewatit SPC 118,
Lewatit SPC 108, K2611, K2621, OC 1501.

5   The properties of these resins, in particular specific
surface area, porosity, stability, swelling or
shrinkage and exchange capacity, can be varied via the
preparation process.

10   In the process according to the invention, the ion
exchange resins can be used in their H form. Preference
is given to using macroporous resins, for example
Lewatit SCP 118, Lewatit SCP 108, Amberlyst A15 or
Amberlyst A35, K2621. The pore volume is from 0.3 to
15   0.9 ml/g, in particular from 0.5 to 0.9 ml/g. The
particle size of the resin is between 0.3 mm and
1.5 mm, in particular between 0.5 mm and 1.0 mm. The
particle size distribution selected may be large or
small. For example, ion exchange resins having very
20   uniform particle size (monodisperse resins) can be
used. The capacity of the ion exchanger, based on the
commercial form, is 0.7 - 2.0 mol/l, in particular 1.1-
2.0 mol/l.

25   The remaining isobutene is reacted with alcohol to give
the corresponding tertiary butyl ether in the
temperature range of 10 - 140°C. The alcohol is used in
excess.

30   In particular, the remaining isobutene is removed by
reaction with methanol to give MTBE. The procedure is
in particular as described in DE 101 02 082. The low-
isobutene C_4 hydrocarbon mixture is fed into the
prereactor together with methanol. A mixture is formed
35   there in which isobutene, methanol and MTBE are at
equilibrium or virtually at equilibrium. This reaction
mixture is passed into the reactive distillation
column.

More methanol may be present in the feed of the
reactive distillation column than is required for the
complete conversion of the isobutene still present.
5   However, the methanol excess should be limited in such
a way that on the one hand there is a sufficient amount
of methanol for the azeotrope of methanol and C_4
hydrocarbons which forms, but on the other hand not so
much that methanol could get into the bottom product,
10   so that on-spec MTBE (methanol content preferably below
5000 ppm by weight) is obtained. However, this only
applies when the oligomers have been removed
beforehand. Otherwise, a mixture of MTBE and oligomers
is obtained.
15

When the methanol content in the column feed is below
the maximum permissible value, additional methanol may
optionally be added. In addition, methanol can be fed
in at the top of the reactive distillation column via a
20   separate apparatus.

In the reactive distillation column, the zone above the
catalyst packing consists of from 5 to 20, in
particular from 10 to 15, plates. The catalyst zone can
25   be estimated as having a distillative action of from 1
to 5 theoretical plates per meter of packing height.
The separating zone below the catalyst comprises from
12 to 36, in particular from 20 to 30, plates.

30   Irrespective of its composition, reaction pressure in
the column and throughput, the temperature of the
column feed is between 50°C and 80°C, preferably
between 60°C and 75°C.

35   Depending on the pressure in the column, the average
temperature in the catalyst zone is preferably from
55°C to 70°C, more preferably from 58°C to 67°C.

The reactive distillation column is operated at pressures, measured at the top of the column, of from 3 bara to 15 bara, preferably from 5 bara to 9 bara, in particular from 7 bara to 8.5 bara.

The hydraulic loading in the catalytic packing of the column is preferably from 10% to 110%, preferably from 20% to 70%, of its flood point loading. The hydraulic loading of a distillation column refers to the uniform flow demands on the column cross section by the rising vapor stream and the refluxing liquid stream. The upper loading limit indicates the maximum loading by vapor and reflux liquid above which the separating action falls as a consequence of entrainment or accumulation of the reflux liquid by the rising vapor stream. The lower loading limit indicates the minimum loading below which the separating action falls or collapses as a consequence of irregular flow or the column running empty, for example the trays. (Vauck/Müller, "Grundoperationen chemischer Verfahrenstechnik [Basic operations of chemical process technology], p. 626, VEB Deutscher Verlag für Grundstoffindustrie.)

At the flood point, the shear stresses transferred from the gas to the liquid are so great that the entire amount of liquid is entrained with the gas in the form of droplets, or that there is phase inversion in the column (J. Mackowiak, "Fluiddynamik von Kolonnen mit modernen Füllkörpern und Packungen für Gas/Flüssigkeitssysteme" [Fluid dynamics of columns having modern random packings and structured packings for gas/liquid systems], Otto Salle Verlag 1991).

The reactive distillation column is operated at reflux ratios of less than 1.5, in particular at those which are greater than 0.4 and less than 1, preferably between 0.5 and 0.9.

The optimum reflux ratio depends on the throughput of the composition of the column feed and on the column pressure. However, it is always within the abovementioned ranges. In the distillate of the reactive distillation, residual isobutene concentrations in the raffinate II (usual term for a mixture of C_4 hydrocarbons freed of 1,3-butadiene and isobutene) of less than 1000 ppm by weight, preferably 500 ppm by weight, most preferably less than 300 ppm by weight (based on the C_4 mixture in the distillate), are obtained.

When the butene oligomers are removed before the reaction with methanol, the bottom product of the reactive distillation column preferably consists of MTBE. It preferably contains less than 2500 ppm by weight of methyl sec-butyl ether and less than 2500 ppm by weight of C_8 hydrocarbons.

The top product of the reactive distillation column may in turn be separated into a C_4 hydrocarbon mixture and methanol, and the C_4 hydrocarbon mixture preferably contains less than 0.5 ppm by weight of MTBE and/or TBA.

The methanol may, for example, be removed by extraction with water. If traces of butadiene have not already been removed before the butene oligomerization, they can be removed from the raffinate II obtained in this way by selective hydrogenation (SHP). The C_4 hydrocarbon mixture obtained from the reactive distillation and optionally freed of methanol may be further separated distillatively. For this purpose, there are two preferred routes:

1. separation into a top fraction which comprises 1-butene and isobutane, and a bottom fraction which comprises n-butane, 2-butenes and any residual amounts of 1-butene. The isobutane can be removed

from the top fraction in a further distillation so that highly pure 1-butene remains, or

2. removal of the isobutane and any further low boilers in a first distillation step, in which 1-
5   butene, 2-butenes and n-butane remain in the bottoms. 1-Butene can be obtained as a low boiler from the bottom product in a further distillation.

10   When alcohols other than methanol are used for the etherification, the parameters of the reactive distillation change correspondingly.

The pure 1-butene prepared in this way contains less than 1000 ppm by weight of isobutene and is in demand
15   as an intermediate. It is used, for example, as a comonomer in the preparation of polyethylene (LLDPE or HDPE) and also of ethylene-propylene copolymers. It also finds use as an alkylating agent and is the starting material for preparing butan-2-ol, butene
20   oxide, valeraldehyde.

A further use of the virtually isobutene-free raffinate II prepared in accordance with the invention is the preparation of n-butene oligomers, in particular by
25   the Octol process.

The hydrocarbons remaining after reaction or conversion of the linear butenes from the raffinate II may optionally be worked up by hydrogenation
30   (CSP = complete saturation process) to give isobutane and n-butane.

The tert-butyl ether occurring as a bottom product in the reactive distillation may be used for various
35   purposes. In addition to the use as a component for gasoline fuels, it finds use, for example, as a solvent. Dissociation of tert-butyl ether provides isobutene of high purity.

In addition to the use as a component in gasoline fuel, the MTBE obtained when methanol is used is, for example, used as a solvent. To obtain MTBE of high purity which is preferably used as a solvent, the

5   bottom product of the reactive distillation obtained in the process may be further purified distillatively. This reduces the content of impurities present in small amounts (for example, methyl sec-butyl ether, C_8-HCs, TBA, alcohols).

10

The dissociation of MTBE to obtain isobutene is described, for example, in DE 100 200 943. The purity of the isobutene obtained is dependent, among other factors, on the proportion of methyl sec-butyl ether in

15   the MTBE. Depending on the requirements, the MTBE used for the dissociation has therefore been prepurified to different degrees of intensiveness.

When the oligomers are not removed before the

20   etherification, the bottom product obtained in the reactive distillation column contains MTBE and the oligomers. This mixture may be used as a fuel component as such or after hydrogenation of the olefinic double bonds. Optionally, this mixture may be fractionated.

25   The individual fractions are then used as already described.

Two embodiments of the process according to the invention are described in detail schematically with

30   the aid of the figures, Fig. 1 and Fig. 2, without limiting the invention to these embodiments. In the schematic diagrams, only the essential stages are shown. For a better overview, the illustration of customary process streams, for example cooling water

35   streams, circulation streams, catalyst recycle streams or recycle streams, and/or customary apparatus, for example heat exchangers or separators, has been dispensed with.

In the process illustrated schematically in Fig. 1, an isobutenic and 1,3-butadienic C_4 hydrocarbon **1** is fed into one or more reactors in which a butadiene hydrogenation is carried out, **2**. Hydrogen **3** is also fed into this reactor for hydrogenation. The reactor effluent is transferred into a next reactor for selective residual butadiene hydrogenation **4**, into which hydrogen is in turn fed **5**. The reactor effluent from **4** is transferred to the reactor for butene oligomerization **6**, in which the isobutene is mainly converted to dimers, trimers and tetramers. The effluent from this reactor is transferred to a distillation column **7** in which the butene oligomers are removed as the bottom product **8**. The stream freed of butene oligomers is conducted via the top of the column **7** into a heat exchanger, in which the condensable constituents are condensed. These are partly recycled into the top of the column **7**. In the heat exchanger, noncondensable constituents are fed to a further use as a gaseous offgas stream **17**. The distillate of the column **7** is fed together with additional methanol **10** into the MTBE fixed bed stage **9**, and the isobutene still present is reacted with it over the fixed bed catalyst to give MTBE. The effluent from the fixed bed stage is fed into a reactive distillation column **11** below the reactive packing **12**. At the bottom of the column, a stream containing MTBE **14** is taken off, while the top product is conducted into a heat exchanger, in which the condensable constituents are condensed as an isobutene-free n-butene stream. These are partly recycled as reflux to the top of the column **11** and discharged from the process as stream **13**. The fractions of the top product which cannot be condensed in the heat exchanger are fed to a further use as a gaseous offgas stream **18**.

The process illustrated schematically in Fig. 2 differs from the process illustrated in Fig. 1 in that, instead of the butadiene hydrogenation **2**, a butadiene removal

15, for example an extractive distillation, is carried out, which removes the majority of the 1,3-butadiene **16** from the isobutenic C_4 hydrocarbon stream **1**. The butadiene-depleted stream from the butadiene removal **15**

5   is subsequently transferred to a reactor for selective residual butadiene hydrogenation **4**, and then further worked up as in Fig. 1.

The examples which follow are intended to illustrate

10 the invention, without narrowing the scope of protection of the patent claims.

Examples

15 The individual process steps for the workup of a crack- C_4 stream (CC_4) were reproduced in the laboratory analogously to the process illustrated in Figure 1.

Example 1 – Selective butadiene hydrogenation

20 An HC mixture having the composition specified in Table 2 is hydrogenated in a fixed bed reactor over a heterogeneous palladium catalyst. In a similar manner to EP 0 523 482, the hydrogenation is carried out in two fixed bed reactors which are operated in series and

25 are each equipped with a separator and a liquid circuit. In each of the liquid circuits is installed a cooler in order to be able to remove the heat of reaction of the hydrogenation.

30 The hydrogen required for the reaction was fed to the reactors in accordance with the amount of 1,3-butadiene to be converted. The LHSV over the entire plant was $8.5 \ t/(m^3h)$.

Percentages of the analyses are to be interpreted as %

35 by mass.

Stage 1	Reactor entrance temperature	29°C
	Pressure	14 bara
	Catalyst	0.5% Pd on Al_2O_3
Stage 2	Reactor entrance temperature	45°C
	Pressure	9 bara
	Catalyst	0.5% Pd on Al_2O_3

Table 2 - Analyses of feed and effluent of the butadiene hydrogenation

	Feed	Stage 1 effluent	Stage 2 effluent
C3-HC [%]	n.d., <0.1	n.d., <0.1	n.d., <0.1
isobutane [%]	2.3	2.3	2.3
n-butane [%]	5.5	5.9	6.3
trans-butene [%]	4.9	17.2	19.7
1-butene [%]	15.9	37.1	40.4
isobutene [%]	24.8	24.8	24.8
cis-butene [%]	4.0	5.1	6.1
1,2-butadiene [%]	0.2	n.d., <0.1	n.d., <0.1
1,3-butadiene [%]	41.4	6.3	0.2
butenyne [%]	0.75	n.d., <0.1	n.d., <0.1
1-butyne [%]	0.2	n.d., <0.1	n.d., <0.1

n.d. = below the detection limit

Example 2 - SHP, further reduction of the 1,3-butadiene content

Residual amounts of 1,3-butadiene which are still present in the C_4 hydrocarbon mixture can be reduced in a further hydrogenation step. The addition of small amounts of carbon monoxide increases the selectivity of the palladium catalyst.

The experiment was carried out with two different raw materials. The feed specified under 2b corresponds to a composition as obtained from the process of Example 1 (hydrogenation of the 1,3-butadiene contained in the

crack-C_4). The feed 2a represents a mixture of C_4 hydrocarbons which is obtained after removal of the 1,3-butadiene from the crack-C_4 (Fig. 2).

The HC mixtures having the composition specified in Table 3 are admixed with 85 ppm of hydrogen and 2 ppm of carbon monoxide. The hydrogenation was effected in a fixed bed reactor under the following conditions:

Temperature:	40°C (isothermal)
Pressure:	13 bara
LHSV:	35 (1/(1*h))
Catalyst:	0.5% of Pd on γ-Al_2O_3 support

Table 3 - Analysis of feed and effluent of the SHP (selective hydrogenation process)

Example	2a feed	2a effluent	2b feed	2b effluent
C3-HC [%]	0.0	0.0	<0.1	<0.1
isobutane [%]	3.9	3.9	2.3	2.3
n-butane [%]	9.5	9.5	5.9	5.9
trans-butene [%]	8.5	8.6	17.6	17.6
1-butene [%]	27.6	27.7	40.9	41.1
isobutene [%]	43.1	43.1	24.8	24.8
cis-butene [%]	6.9	6.9	8.2	8.2
1,2-butadiene [ppm]	<100	n.d.	<1	n.d.
1,3-butadiene [ppm]	2176	3	1960	2
butenyne [ppm]	n.d.	n.d.	12	n.d.
1-butyne [ppm]	n.d.	n.d.	56	n.d.

n.d. = below the detection limit

Example 3 - Isobutene oligomerization and distillation
The isobutene was oligomerized in a tubular reactor of length 200 cm (wound to a spiral), internal diameter 6 mm. The tube is heated externally by an oil bath. The catalyst used was 54 ml of Amberlyst 15 from Rohm & Haas. Before use, the catalyst was washed with water, then with methanol. The reactor was operated at a

constant 22 bara using a pressure regulator at the reactor exit. After startup, the experimental plant was operated for 24 hours and the product was discarded. Afterwards, the product of the plant was collected over 100 hours and distilled in a laboratory column. The fractions obtained were analyzed by gas chromatography. Table 4 lists the process conditions, reactant compositions and the analyses of the C_4 and the C_8 fraction. In the table,

- Isobutene conversion: proportion of isobutene which was converted in the reactor.
- C_8 selectivity: selectivity at which C_8 hydrocarbons (dimers of the butenes) were formed in the reaction.
- The value quoted for 2,4,4-trimethylpentene under C_8 analysis states the proportion (percentage by mass) of the dimers of isobutene in the C_8 fraction.

Two experiments (3a, 3b) were carried out with feeds of different composition. In each experiment, fresh catalyst was used.

Table 4 - Reaction conditions and analysis of the isobutene oligomerization

Experiment No.		3a	3b
Heating bath temp.	(°C)	62.5	62.5
Reactor feed	(kg/h)	0.300	0.306
Feed analysis			
propene	(%)	0.01	0.00
isobutane	(%)	2.22	2.07
n-butane	(%)	10.32	9.20
trans-butene	(%)	25.83	9.21
1-butene	(%)	2.92	27.10
isobutene	(%)	45.84	46.12
cis-butene	(%)	12.67	5.825
remainder	(%)	0.20	0.48
Effluent analysis, C4 fraction (normalized to 100% of C4)			
isobutane	(%)	4.16	3.74
n-butane	(%)	17.41	15.77
trans-butene	(%)	42.41	16.84
1-butene	(%)	4.84	42.67
isobutene	(%)	11.71	9.75
cis-butene	(%)	19.21	10.66
remainder	(%)	0.25	0.58
Isobutene conversion	**(%)**	**84.33**	**87.38**
C8 selectivity	(%)	77.82	77.91
Analysis of the C8 fraction (normalized to 100% of C8)			
2,4,4-tri-Me-pentene	(%)	91.40	92.60

5 **Example 4 - Isobutene oligomerization over semi-neutralized ion exchanger**

*a)   Preparation   of   a   semineutralized   catalyst,
    adjustment of the acid capacity*

10

The Amberlyst 15 ion exchanger from Rohm and Haas used had an original acid capacity of 1.7 mol of H^+/l. To

adjust the activity to that desired, 40% of the acidic centers were neutralized.

For this purpose, 1000 ml of the ion exchange resin
5   were slurried in 1000 ml of deionized water and a solution of 27.2 g of sodium hydroxide (0.68 mol) and 500 ml of deionized water were added dropwise with stirring in the temperature range from 20 to 40°C within one hour. Stirring was continued for 5 min and
10   the ion exchange resin was then washed to neutrality with three times 1000 ml of deionized water. The subsequent capacity measurement of the partly neutralized ion exchanger gave 1.00 +/- 0.03 mol of H^+/l. The catalyst was dried at 70°C for 15 h before
15   use.

b) Oligomerization
The isobutene was oligomerized in a similar manner to Example 3. 51 ml of the semineutralized ion exchanger
20   were used. The reactor was operated at 22 bara. After an activation phase of 24 hours, the effluent of the reactor was analyzed by gas chromatography. Table 5 lists the process conditions, reactant compositions and the analysis, separated into the C_4 and the C_8 fraction.
25

Two experiments (4a, 4b) were carried out using feeds of different composition. In each experiment, fresh catalyst was used.

Table 5 - Reaction conditions and analysis of the isobutene oligomerization

Experiment No.		4a	4b
Heating bath temp.	(°C)	100	100
Reactor feed	(kg/h)	0.509	0.480
Feed analysis			
propene	(%)	0.00	0.00
isobutane	(%)	2.75	0.04
n-butane	(%)	8.52	13.85
trans-butene	(%)	8.98	17.23
1-butene	(%)	29.00	19.17
isobutene	(%)	44.40	40.00
cis-butene	(%)	5.76	9.37
remainder	(%)	0.60	0.35
Effluent analysis, C4 fraction (normalized to 100% of C4)			
isobutane	(%)	3.41	0.06
n-butane	(%)	10.80	20.17
trans-butene	(%)	12.31	26.33
1-butene	(%)	34.07	24.15
isobutene	(%)	30.45	14.18
cis-butene	(%)	8.37	14.77
remainder	(%)	0.60	0.35
Isobutene conversion	**(%)**	**45.16**	**75.22**
C8 selectivity	(%)	87.71	78.01
Analysis of the C8 fraction (normalized to 100% of C8)			
2,4,4-tri-Me-pentene	(%)	94.48	90.53

5 **Example 5 - MTBE synthesis in fixed bed reactors**

For the experiments, a construction similar to the isobutene oligomerization was used. The reactor consisted of a tube wound into a spiral which was heated externally by an oil bath. The front portion
10 (approx. the first quarter) of the reactor was not charged with catalyst, in order to preheat the feed to the desired temperature. In experiment 5a, the back

portion was charged with 125 ml of ion exchanger, and in experiment 5b with 94 ml of ion exchanger. The reactor was heated isothermally by the oil bath to 50°C.

5   The catalyst used was Amberlyst 15. The pressure of the plant was 8 bara.

The feed used was the C_4 fractions from Example 3. Analyses and feed amounts are specified in Table 6. Percentages are to be interpreted as % by mass.

10

Table 6 - Feeds and analyses of the MTBE fixed bed experiments

		Experiment 5a		Experiment 5b	
C4 feed	(g/h)	100		100	
methanol feed	(g/h)	7.7		6.4	
		Feed analysis	Effluent analysis	Feed analysis	Effluent analysis
methanol	(%)	7.15	1.26	6.03	1.11
isobutene	(%)	10.87	0.57	9.15	0.57
MTBE	(%)	0.00	16.19	0.00	13.50
n-butane	(%)	16.19	16.17	14.81	14.82
isobutane	(%)	3.84	3.86	3.52	3.51
1-butene	(%)	4.48	4.49	40.07	40.10
cis-butene	(%)	17.84	17.84	10.04	10.02
trans-butene	(%)	39.38	39.39	15.82	15.83
remainder	(%)	0.24	0.23	0.56	0.55

15 **Example 6 a - Reactive distillation**

The schematic construction of the reactive distillation column is reproduced in Figure 1 and 2. The diameter of the column was 312.7 mm. In the upper portion of the column, approx. 2 m of Montz-Pak A3-500 were installed

20   as a rectifying section. Below this, likewise in the rectifying section of the column, were disposed approx. 11.4 m of Katapak-SP 12. The lower section of the column consisted of approx. 3.6 m of Montz-Pak A3-500.

The feed position was disposed in the upper third of the lower Montz-Pak A3-500.

The catalyst used in the Katapak-SP 12 was Amberlyst 15. The pressure of the apparatus was 7.5 bara.

5   The feed for the column was a mixture made up of product streams of an industrial scale plant. The isobutene, MTBE and methanol concentrations were set substantially identically to those of the effluents of the laboratory reactors from Example 5. The composition

10   of the remaining C_4 hydrocarbons is comparable to the effluents of the laboratory reactors from Example 5.

The feed rate was 700 kg/h. A reflux ratio of 1.09 was set. 578.8 kg/h of distillate and 121.2 kg/h of bottom product were obtained. Percentages are to be

15   interpreted as % by mass.

The isobutene content measured in the distillate was 136 ppm.

Experiment 6a		Feed analysis	Distillate analysis	Bottoms analysis
methanol	(%)	1.26	1.14	0.00
isobutene	(%)	0.57	0.01	0.00
MTBE	(%)	16.19	0.00	95.82
n-butane	(%)	14.17	17.24	0.01
isobutane	(%)	4.995	6.08	0.00
1-butene	(%)	7.855	9.57	0.00
cis-butene	(%)	16.84	20.49	0.03
trans-butene	(%)	37.39	45.48	0.03
remainder	(%)	0.73	0.00	4.11

20   **Example 6 b - Reactive distillation**

In the same reactive distillation plant as described in Example 6 a, an experiment was carried out with a reactant stream of different composition.

The catalyst used was likewise Amberlyst 15. The

25   pressure of the apparatus was 7.5 bara.

The feed rate was 700 kg/h. A reflux ratio of 1.09 was set. 595.5 kg/h of distillate and 104.5 kg/h of bottom

product were obtained. Percentages are to be interpreted as % by mass.

An isobutene content in the distillate of 102 ppm was measured.

Experiment 6b		Feed analysis	Distillate analysis	Bottoms analysis
methanol	(%)	1.11	0.93	0.00
isobutene	(%)	0.57	0.01	0.00
MTBE	(%)	13.50	0.00	96.28
n-butane	(%)	12.84	15.09	0.01
isobutane	(%)	5.49	6.46	0.00
1-butene	(%)	36.77	43.23	0.01
cis-butene	(%)	11.13	13.07	0.03
trans-butene	(%)	18.05	21.21	0.02
remainder	(%)	0.55	0.00	3.65

The reference numerals in Fig. 1 and Fig. 2 have the following meanings:

1.   Isobutenic C_4 hydrocarbon stream
2.   Butadiene hydrogenation
3.   Hydrogen
4.   Selective residual butadiene hydrogenation
5.   Hydrogen
6.   Butene oligomerization
7.   Distillation for oligomer removal
8.   Butene oligomers
9.   MTBE fixed bed stage
10. Methanol
11. Reactive distillation column
12. Reactive packing of the reactive distillation column
13. Isobutene-free n-butene stream
14. MTBE
15. Butadiene extraction
16. Butadiene
17. Offgas stream

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18.   Offgas stream